



ARMY INSTITUTE OF PUBLIC HEALTH

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# **Quantitation and Ratio Determination of Uranium Isotopes in Water and Soil Using Inductively Coupled Plasma Mass Spectrometry (ICP-MS)**

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# Introduction

- ✦ **Uranium – overview**
- ✦ **Sample prep:**
  - water – EPA 3020**
  - Soils – EPA 3052 (modified)**
- ✦ **Analysis – ICP-MS**
  - water – EPA 200.8**
  - soils – EPA 6020**
  - Quality Controls**
- ✦ **ICP-MS and  $\alpha$ -Spec**
- ✦ **Summary**
- ✦ **Questions**

# Introduction

- ✦ Ubiquitous element
- ✦ Naturally Occurring U Isotopes:  
234 (0.0055%, 0.245 E6 yr.), 235 (0.72%, 703 E6 yr.), 238 (99.275%, 4,468 E6 yr.)
- ✦ Natural U235/238 atomic Ratio:  $7.2 \times 10^{-3}$
- ✦ Natural U234/238  $\alpha$  activity Ratio: 1 (secular equilibrium)
- ✦ Used for fuel in atomic energy and warfare
- ✦ Depleted Uranium DU: 235 Isotope Quantity Reduced  
U235/238 atomic Ratio:  $2 \times 10^{-3}$

# Sample Preparation

- ✦ **Water - EPA 3020**  
Acid digestion
- ✦ **Soils – EPA 3052 (modified)**  
Acidic microwave digestion  
Complete digestion
- ✦ **Ratio – Depends on Matrix (see methods above)**

# Sample Analysis ICP-MS

- ✦ **Water - EPA 6020**
- ✦ **Soils – EPA 200.8**
- ✦ **Ratios – In house Method**

# Sample Analysis QC

- ✦ **Sample Duplicates – precision check**
- ✦ **Blanks – contamination check**
- ✦ **Laboratory Control Samples – accuracy check**
- ✦ **Matrix Spikes – matrix effect**
- ✦ **\*Mass bias correction standard**



# Analysis Recovery QC

	Water	Soil	Ratio
Duplicates	---	$\leq 20\%$ RPD	---
Blanks	< RL	< RL	---
LCS	$\pm 15\%$	$\pm 20\%$	---
MS	$\pm 30\%$	$\pm 30\%$	---
Inst Spike	$\pm 20\%$	$\pm 20\%$	---
ISA / ISB	---	$\pm 20\%$	---

# Common Analysis Techniques

✦ **α Spectroscopy**

✦ **ICP-MS**

## **$\alpha$ Spectroscopy**

- ✦ **Measures 234 and 238 isotopes**  
U-234 from the Uranium Decay Series  
U238  $\rightarrow$  Th234  $\rightarrow$  Pa234  $\rightarrow$  U234  $\rightarrow$  Th230  $\rightarrow$  .....
- ✦ **Sample preparation required (matrix removed)**
- ✦ **Tracer added for quantification**
- ✦ **Measure  $\alpha$  particles from radioactive decay**
- ✦ **Ratio and Concentration in same analysis**
- ✦ **Detection limits – depends on count time**

## ICP- MS

- ✦ **Measures 235 and 238 isotope ions**  
235 from the Actinium Decay Series  
U235 → Th231 → Pa231 → Ac227 → .....
- ✦ **Sample preparation**
- ✦ **Count ions**
- ✦ **Conc. and Ratio: two different analyses**
- ✦ **Detection limit: matrix and instrument**

## ICP- MS 235/238 Ratio Comparison

Uncorrected Bias	Corrected Bias
6.51 x10 <sup>-3</sup>	7.24 x10 <sup>-3</sup>
6.82 x10 <sup>-3</sup>	7.18 x10 <sup>-3</sup>
6.58 x10 <sup>-3</sup>	7.25 x10 <sup>-3</sup>
6.24 x10 <sup>-3</sup>	7.14 x10 <sup>-3</sup>
6.74 x10 <sup>-3</sup>	7.22 x10 <sup>-3</sup>

Accepted Ratio value 7.26 x10<sup>-3</sup>

## ICP- MS

- ✦ **Measures 235 and 238 isotope ions**  
235 from the Actinium Decay Series  
U235 → Th231 → Pa231 → Ac227 → .....
- ✦ **Sample preparation**
- ✦ **Count ions**
- ✦ **Conc. and Ratio: two different analyses**
- ✦ **Detection limit: matrix and instrument**

# Choices

✦  **$\alpha$  Spectroscopy**

✦ **ICP-MS**

✦ **Questions you need answered:**

**Concentration?**

**Ratio?**

## ICP- MS and $\alpha$ Spec

ICP-MS	$\alpha$ Spec
235 Conc. Sufficient for ratio	Long count time
Ratio & Conc. Separate Analysis	Ratio & Conc. Same Analysis
Correct ratio? – bias, conc.	Correct ratio – recoil effect
100 mL sample	1 L sample



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EMDQ**

# Questions

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